A Study of Some Cerium Compounds

THESIS

Presented to the Faculty of the College of Arts, Philosophy and Science of the Ohio State University for the Degree of Doctor of Philosophy

BY

CLARENCE CHARLES VOGT

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Dissertation

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I. HISTORICAL SKETCH.

1. THE DISCOVERY OF CERIUM.

Cerium was discovered in the year 1803 by Klaproth[1] and, independently, by Berzelius and Hisinger[2] while working with an ore from Sweden. On account of the light brown color of the oxide obtained, Klaproth named the new substance ochroite. Berzelius and Hisinger gave it the name cerium, in honor of the discovery of the asteroid Ceres, in 1801. What these investigators had discovered was the cerium earths, consisting of cerium, lanthanum, neo- and praseo-dymium, samarium, europium and gadolinium. The honor for the actual discovery of the element cerium belongs to Mosander, since he, in the year 1839, was the first to separate cerium from the other earths.[3]

2. THE OCCURRENCE OF CERIUM.

Cerium is always found associated with the other rare earths and always occurs in the combined state. These earths are very wide-spread in traces, but extensive deposits of their characteristic minerals occur only in definite localities. The more important of these minerals are monazite, ((Ce, La, Di) PO_4 39-74 per cent cerium earths), cerite, [(Ca, Fe) (CeO) (Ce_2.3OH) $(SiO_3)_8$] 36-72 per cent cerium earths) and allanite or orthite, (HR″ R_3''' Si_3 O_{13}) 2-34 per cent cerium earths). These minerals are found principally in the Scandinavian Kingdom, the Ural Mountains, Brazil, Germany; and in the United States, in North and South Carolina, Virginia, Texas, Colorado and Idaho.

The wide-spread character of cerium may be shown by its presence in granite,[4] apatite, pyromorphite, marble,[5] scheelite,[6] Scottish strontianite,[7] and in serpentine [8]. Hillebrand, in his "Analysis of Silicate and Carbonate Rocks," calls attention to a sample of piedmontite from Maryland which contained over two per cent of cerium.

Cossa[9] [10] [11] has proved the presence of cerium in plant ashes, in bone ashes, and in urine. Young[12] and, subsequently, Lockyer[13] announced the discovery of cerium lines in the solar spectrum, but this has been questioned by later observers.[14]

3. THE EXTRACTION OF CERIUM FROM ITS ORES.

Cerium plays the part of a base in the various phosphates and silicates which constitute its ores. Like analogous aluminium compounds, these materials are decomposed by prolonged digestion with concentrated sulphuric acid. The finely ground mineral is heated for a long time with sulphuric acid, the excess of acid being volatilized from the mixture toward the end of the process. The cooled mass is then extracted several times with cold water, in order to completely dissolve the soluble sulphates formed during the process of the digestion. The rare earths occur in the analytical group with iron and aluminium. Their separation from these metals is affected by their precipitation with either oxalic acid or ammonium oxalate in acid solution.

The double potassium sulphates of the cerium group of the rare earths are insoluble in a saturated solution of potassium sulphate, while those of the yttrium group are soluble under the same conditions. This fact forms a ready basis for the division of the rare earths into two groups. Finely pulverized potassium sulphate is slowly added to a concentrated solution of the sulphates of the rare earths. The double potassium sulphates of the cerium earths are precipitated, while those of the yttrium earths remain in solution. The addition of potassium sulphate must be continued until no more of the salt dissolves in the solution. The precipitated double potassium sulphates include those of cerium, lanthanum, neo- and praseo-dymium, samarium, gadolinium and europium, known collectively as the cerium earths.

None of the methods employed for the separation of cerium from the other cerium earths are quantitative, and all require repeating. The number of repetitions depends upon the relative quantity of cerium present in comparison with the quantities of the other cerium earths. The separations are all based upon the oxidation of cerous salts to the ceric state, and upon the properties of the ceric compounds obtained in this way. A statement of the more important methods follows.

(*a*) *Treatment of the ignited oxides with nitric acid.*

When the cerous salts of the oxyacids are ignited, they decompose forming the slightly basic cerium dioxide. Under similar conditions the oxyacid salts of the other cerium earths, on the contrary, form the more pronouncedly basic sesquioxides. Therefore, when a mixture of the oxides of the cerium earths obtained by ignition is treated with dilute nitric acid, the basic sesquioxides dissolve leaving behind impure cerium dioxide.[15] [16] This method is employed in the rough separation of cerium on the large scale.

(b) The oxidation of the hydroxides with chlorine gas.

The hydroxides of the cerium earths are suspended in a potassium hydroxide solution. Chlorine gas is then allowed to bubble through this solution. The cerous hydroxide is oxidized by this treatment to the less basic ceric hydroxide. The ceric hydroxide remains insoluble, provided the solution is kept alkaline by the addition of potassium hydroxide from time to time. The other more pronouncedly basic hydroxides are dissolved, either as chlorides or as hypochlorites.[17] [18] This method is adapted to the extraction of small quantities of cerium.

(c) Fusion with potassium nitrate.

The mixed oxides are fused with from eight to ten times their weight of potassium nitrate. The mixture is heated to 300°-350° until the evolution of nitric oxide begins.[19] Under these conditions, the cerium dioxide is converted into basic ceric nitrate, which is much less soluble in water than the nitrates of the other members of this group.

The fused mass is cooled, pulverized, and then extracted with water. The insoluble part is next treated with a dilute solution of nitric acid in order to remove the more soluble nitrates as completely as possible. This leaves the undissolved ceric salt in an impure state. Sodium nitrate is sometimes added to the fusion mixture to lower the temperature necessary for melting.[20] The fusion process is of interest only from an historical standpoint, since it is no longer in practical use.

(d) Method based upon hydrolysis.

The success of this method is due to the tendency of ceric salts to undergo hydrolysis, owing to the very slightly basic character of tetravalent cerium. The mixture of the oxides is dissolved in concentrated nitric acid. The cerium dioxide is converted into the tetravalent ceric nitrate by this treatment, while the other members of the group form trivalent metallic nitrates. After the solution has been evaporated to a small bulk, a considerable quantity of boiling water is added in order to precipitate the basic ceric nitrate owing to the tendency of the ceric salts to hydrolyze. A part of the cerium remains in the solution along with the other earths, but the precipitate is almost pure cerium. Brauner[21] has made a quantitative study of this process, using small quantities. He states that about eighty-one per cent of the cerium present can be extracted in a single operation.

Several investigators have worked along similar lines with the sulphate. The hydrolytic decomposition of the sulphate is markedly less than the decomposition of the nitrate. Therefore, the use of the nitrate

is the more advantageous. The method just described is well adapted for use on the large scale. It is easily carried on and is very economical.

(e) Fractional crystallization with ammonium nitrate.

The limited solubility of ceric ammonium nitrate in concentrated nitric acid forms the basis for this separation.[22] [23] The mixed oxides are dissolved in concentrated nitric acid. To the nitric acid solution is added one-half of its volume of water together with a concentrated solution of ammonium nitrate (100 grams of ammonium nitrate to 100 grams of the mixed oxides). After the solution has been evaporated until crystals begin to appear on the surface, it is allowed to cool and to crystallize at room temperature. The crystals which separate are dried and are then recrystallized from a concentrated nitric acid solution. Various modifications[24] [25] of this method have been suggested.

Owing to the numerous recrystallizations necessary, a considerable quantity of cerium is left in solution in this method. However, the process can be conducted to advantage on the large scale, by systematic operations and it enjoys a wide practical usage.

(f) Oxidation with ammonium persulphate.

The oxidation of a cerous salt and its precipitation as a basic ceric salt are effected in a single operation in this method. The separation depends upon the oxidizing power of ammonium persulphate and upon the hydrolysis of the ceric salt formed, in a neutral or slightly acid solution. A concentrated solution of ammonium persulphate is slowly added to a boiling solution of cerous sulphate or, better, cerous nitrate. Some scheme, such as the addition of calcium carbonate or sodium acetate, is used in order to keep the solution as nearly neutral as possible. The cerium is precipitated as basic ceric sulphate or nitrate.[26] [24] This process is of advantage when dealing with the separation of cerium on a limited scale.

(g) Oxidation with hydrogen peroxide.

This method also includes the oxidation and the precipitation of the cerous salt in one operation. It is based upon the oxidizing power of hydrogen peroxide in a slightly alkaline solution and upon the instability of ceric acetate in a boiling solution. A solution of hydrogen peroxide, free from phosphoric acid, and magnesium acetate is added to a boiling neutral solution of cerous nitrate.[27] The cerium precipitates as a basic ceric acetate, in a fairly pure condition. This method precipitates the cerium completely, along with small quantities of the other earths. It is an excellent process for the purification of small quantities of cerium.

(h) Oxidation with potassium permanganate.

Cerous salts are oxidized by potassium permanganate only in the presence of a base. Under these conditions, the ceric salt which is formed is decomposed and ceric hydroxide is precipitated. Quite a wide range of bases, such as mercuric oxide,[28] zinc oxide,[29] and magnesium oxide[30] have been effectively employed in this process. James,[31] in a critical review of the method, gives directions essentially as follows. To a solution of the double ammonium nitrates of the cerium earths is added an excess of potassium permanganate in order to convert the cerous salt into the ceric salt. Next, sufficient zinc oxide, suspended in water, is added to precipitate incompletely the ceric salt as ceric hydroxide. The separation of the cerium from any excess of the base used and from the manganese, which was precipitated during the oxidation, is easily effected. The entire precipitate is dissolved in hydrochloric acid and oxalic acid is then added to the solution in order to precipitate the cerous chloride as cerous oxalate. This method is easily operated and is well adapted for separation, either on the small or the large scale.

4. THE ATOMIC WEIGHT OF CERIUM.

As late as the year 1860, nothing was known of the absorption spectrum test for the purity of cerium. Consequently, the determinations of the atomic weight of cerium prior to that time are untrustworthy. In 1860 it was discovered that solutions of pure cerium salts show no absorption spectrum lines. This discovery furnished a convenient and an accurate test for the purity of cerium preparations. Since that time, the determination of the atomic weight of cerium has been the object of numerous investigators.

The principal methods employed have been the determinations of the following ratios:

$Ce_2(SO_4)_3 : Ce_2O_4$, $Ce_2(SO_4)_3 : BaSO_4$,
$Ce_2(C_2O_4)_3 : Ce_2O_4$, $Ce_2(SO_4)_3.8H_2O : Ce_2O_4$,
$Ce_2(C_2O_4)_3 : 6CO_2$, $CeCl_3 : 3Ag$.
$Ce_2(C_2O_4)_3 : 3C_2O_3$,

The value given by the International Atomic Weight Commission for 1909 is 140.25. Brauner,[33] in a critical review of the work done on the atomic weight of cerium, states that this figure is very nearly the true value. There is only a slight uncertainty in regard to the second decimal figure. For a bibliography of the literature see Meyer.[33]

5. TYPICAL CERIUM COMPOUNDS AND THEIR CHARACTERISTICS.

Cerium forms two classes of compounds: the cerous, in which the metal is trivalent, and the ceric, in which it is tetravalent.

The cerous salts are the more stable and for this reason, they are the more familiar and numerous. In general they are colorless. Suitable oxidizing agents convert the cerous into the ceric salts.

The ceric salts are unstable, since they readily undergo hydrolysis or reduction. They are yellow to red in color. With the ordinary reducing agents the ceric salts are easily brought to the trivalent condition.

Cerium also has the ability to form a hydrated peroxide of the formula $Ce(O_2H)(OH)_3$, when treated with hydrogen peroxide in an ammoniacal solution.

(a) Typical Cerous Compounds.

The trivalent cerous compounds are very similar to those of aluminium. Cerous hydroxide is, however, a much stronger base than aluminium hydroxide, and this occasions some difference in the properties of corresponding salts. Neutral solutions of cerous salts can be boiled without undergoing hydrolysis to any marked extent, provided oxidation is prevented. Cerous hydroxide is not soluble in an excess of caustic alkali. No compounds have been prepared in which trivalent cerium functions as an acid forming element. The cerous salts, in general, are highly hydrated.

Cerium, in common with the other rare earths, does not possess the ability of forming alums, but it is able to form several double sulphates of other types with the alkali metals and ammonium. These salts differ, both in crystalline structure and in the number of molecules of water of crystallization, from the alums. A statement of some of the more common cerous compounds and some of their properties follows.

(1) Cerous Oxide, Ce_2O_3.

The actual isolation of this compound is very difficult. The question of its preparation is a mooted one at the present time. Efforts have been made to prepare this oxide by the ignition of the cerous oxyacid salts, in the presence of a reducing agent. The product obtained in this way has been described as the sesquioxide of cerium, but this has been sharply criticised.[34 35 36 37 30 38]

(2) Cerous Chloride, $CeCl_3$.

This compound is capable of existence both in the anhydrous form and also associated with 7 or $7\frac{1}{2}$ molecules of water of crystallization.

Like anhydrous aluminium chloride, the analogous cerous chloride cannot be prepared by the dehydration of the salt containing crystal water. The anhydrous compound may be obtained by the decomposition

of the double chloride of cerium and ammonium by heat. The general methods for the preparation of anhydrous chlorides, by the action of either sulphur monochloride or carbon tetrachloride or carbon and chlorine upon the oxide, are applicable to the preparation of anhydrous cerous chloride. The salt may also be prepared by the action of chlorine gas at a high temperature upon a suitable cerous compound.[39 40 20 41 42]

The hydrated salt is prepared by the evaporation of a solution of cerous chloride. The solution of either cerous carbonate or cerous hydroxide in hydrochloric acid is the usual method for the preparation of the chloride solution. The question of the number of molecules of water of crystallization present in this salt is much debated, and is unsettled at the present time. When the hydrated chloride is heated in the air an oxychloride, CeOCl, is found.[17 43 44 45 46 47 48 49 50 51 54 53]

Cerous chloride, like the chlorides of the other members of the cerium group, readily forms double chlorides with the chlorides of the less positive metals such as mercury, gold and platinum.[39 54 55 56 57 58 59 60]

(3) Cerous Sulphide, Ce_2S_3.

Cerous sulphide cannot be prepared in solution by precipitation methods, owing to its ready hydrolysis. However, when it has once been obtained by other methods, it is very stable in the air. Unlike aluminium sulphide this compound undergoes complete hydrolysis very slowly, even in a boiling solution. It is usually prepared by fusion methods.

Cerous sulphide dissolves readily in dilute acids, with the evolution of hydrogen sulphide. When ignited, it burns vigorously forming a mixture of ceric oxide and cerous sulphate.[61 46 62 40 53 38]

(4) Cerous Sulphate, $Ce_2(SO_4)_3$+4, 5, 8, 9, or 12 H_2O.

When a dilute solution of sulphuric acid is added to cerous carbonate or hydroxide, a colorless solution of cerous sulphate is obtained. The ratio of water of crystallization present in the salt obtained by the evaporation of this solution depends upon the temperature of crystallization. In general, the quantity of water of crystallization varies inversely as the temperature at which crystallization takes place. However, according to the solubility measurements of Koppel[63], the 9-hydrate is less soluble and therefore more stable than the 8-hydrate between 30° and 41°.

The 12-hydrate is stable below 3°, and its solubility increases with the temperature. Between 3° and 30° the 8-hydrate is the stable form, but its solubility decreases very rapidly with an increase of temperature. As has been stated from 30° to 41° the 9-hydrate becomes the stable salt. Its solubility also varies inversely as the temperature, but the change per degree is not so great as for the 8-hydrate. The 4-hydrate becomes the more stable at 41°, and this is the salt which is obtained by the crystallization of a boiling solution of cerous sulphate. Its solubility also decreases with an increase of temperature. The 5-hydrate is

metastable throughout its whole possible range of existence, from 45° to 100°. The solubility of the hydrated cerous sulphate varies between the limits of 16.56 gr. $Ce_2(SO_4)_3$ in 100 gr. of water in the case of the 12-hydrate at 0° to .43 gr. $Ce_2(SO_4)_3$ in 100 gr. of water at 100.5°.[39 64 65 66 57 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81]

The peculiarities exhibited by these hydrates seemed to warrant the preparation of some of the closely related sulphonates and a study of their properties.

Cerous sulphate possesses the power of forming double sulphates with the alkali metals and ammonium. These double salts are not so highly hydrated as the alums. They are even less soluble than the alums. Their insolubility in a concentrated solution of potassium sulphate has already been mentioned, in the separation of the cerium from the yttrium earths. Cerous sulphate also forms double sulphates with the sulphates of a few of the divalent metals.[61 82 77 83 39 84 85 86 87]

(5) Cerous Nitrate, $Ce(NO_3)_3.6H_2O$.

Cerous nitrate is usually prepared by the double decomposition of solutions of barium nitrate and cerous sulphate. It may also be prepared by the action of nitric acid, in the presence of a reducing agent, upon ceric salts. The well-known method of dissolving cerous carbonate or hydroxide in dilute nitric acid is also frequently employed. When a solution of cerous nitrate is evaporated to a sirupy consistency and is then allowed to cool, radiating crystals of the hydrated salt are formed.[39 40]

The most characteristic property of cerous nitrate is its ability to form double nitrates with potassium and ammonium. In addition, the nitrates of the divalent metals readily combine with cerous nitrate forming double salts. All of these compounds are soluble in water, but only very slightly soluble in nitric acid.[86 87 50 46 88 89]

(6) Cerous Carbonate, $Ce_2(CO_3)_3.5H_2O$.

Cerium differs from the more common trivalent metals in its ability to form a carbonate in water solution. When a soluble cerous salt is treated with a soluble carbonate, insoluble cerous carbonate is precipitated. This salt is not hydrolyzed to any considerable extent, even on long standing. This reaction again illustrates the basic character of the cerous ion.[44 40 90] Cerous carbonate dissolves in an excess of alkali carbonates, forming double carbonates.

(7) Cerous Oxalate, $Ce_2(C_2O_4)_3 9$ or $10\ H_2O$.

White crystals of this compound are precipitated, when a solution of ammonium oxalate or oxalic acid is added to a neutral or acid solution of a cerous salt. This reaction is of considerable importance, since it is the one which constitutes the basis for the separation of cerium from the more common members of the iron group of metals. The quantity

of water of crystallization present in the compound is a debated question. Meyer[91] assigns the formula $Ce_2(C_2O_4)_3.10H_2O$ to the compound. Hauser and Wirth,[92] in a recent study of the solubility of the oxalates of the rare earths, seem to prefer the ratio of nine molecules of water.

(*b*) *Typical Ceric Compounds.*

Owing to the ease with which the ceric compounds undergo either hydrolysis or reduction, they are much less stable than the cerous compounds. The weakly basic character of the ceric ion accounts for the pronounced tendency of its salts to hydrolyse. Only the strongest acids are able to form neutral salts with tetravalent cerium.

Although the basic character of cerium is extremely weak, its acid-forming character is yet weaker. Ceric hydroxide is insoluble, even in concentrated solutions of the hydroxides of the alkali metals. This fact illustrates the very weakly acid property of the ceric ion. Some of the more important ceric compounds will now be discussed.

(1) Cerium Dioxide, CeO_2.

The product formed, when a cerous salt of an oxyacid is ignited or when the metal is burned in the air, is cerium dioxide.[17 93 94 95 96 37 40 68 79 80 45 97 98 59 100 101 102 103 104 24 105 106 38 107 108 31] This compound is insoluble in nitric or hydrochloric acids, unless a reducing agent is present. Dilute sulphuric acid is also without effect upon cerium dioxide. Concentrated sulphuric acid, on the contrary, converts it directly into the anhydrous ceric sulphate. Cerium dioxide is very stable and is difficult to reduce.

(2) Ceric Chloride.

Ceric chloride is incapable of existence alone. But in a solution of hydrochloric acid it forms the chloroceric acid, H_2CeCl_6, typical of the tetravalent metals. It is worthy of notice that cerium acts as an acid forming element in this case, when in the presence of one of the strongest acids. The pyridine salts of chloroceric acid have been prepared.[109]

(3) Ceric Sulphate, $Ce(SO_4)_2$ or $Ce(SO_4)_2.4H_2O$.

Anhydrous ceric sulphate is formed by the action of concentrated sulphuric acid upon cerium dioxide. The hydrated salt is formed by the solution of cerium dioxide or ceric hydroxide in moderately concentrated sulphuric acid. A ceroceric sulphate is first obtained when this solution is evaporated and then the red crystals of the ceric sulphate separate out.

This salt exhibits a marked tendency toward hydrolysis. The neutral salt exists in solution only when there is also present a considerable excess of free acid. Upon dilution or upon boiling, a basic ceric sulphate begins to precipitate.[70 77 37 68 36 88 110 111 112 113 114 76]

Cerium differs from the most of the tetravalent elements in its ability to form double sulphates with the alkali metals and ammonium. These salts are very difficultly soluble in water.[70 115 77 370 116]

(4) Ceric Nitrate, $Ce(NO_3)_3OH.3H_2O$.

A basic nitrate of tetravalent cerium is obtained, when ceric hydroxide is dissolved in concentrated nitric acid. The neutral salt has not been prepared, even in the most strongly acid solutions. The solution of the basic salt is strongly acid, and undergoes further hydrolysis when it is warmed or diluted.[117 118]

Tetravalent cerium forms double nitrates both with ammonium nitrate and with the nitrates of many of the divalent metals. Meyer states that in alcoholic solutions, the complex $Ce(NO_3)_6$ forms a divalent ion. Both the ceric ammonium nitrate and the ceric magnesium nitrate are largely employed in the commercial purification of cerium compounds.[22 119 120 64 121 86 122 88 111]

(*c*) *Cerium Peroxide Compounds.*

When ammonium hydroxide and hydrogen peroxide are added to a solution of any cerium salt, a hydrated peroxide of the formula, $Ce(O_2H)(OH)_3$, separates as a yellow precipitate. This reaction is taken advantage of as an analytical test for the detection of very small quantities of cerium.[77 123 124 125 126 127]

II. THE OBJECT OF THE STUDY.

The object of the study was threefold.

1. The first object was an investigation of the various methods employed in the extraction of cerium from its ores and its subsequent purification. It was hoped that certain steps might possibly be improved.

2. The second object was, originally, the preparation of pure cerous oxalate and a study of this compound with respect to its hydrates and their solubilities. A similar study of lanthanum oxalate was also planned. But, on account of the publication of the first of a series of studies on the oxalates of the rare earths by Hauser and Wirth,[92] this study was abandoned.

3. The third object was the preparation of the cerous sulphonates of benzene and some of its derivatives. A study of the properties of these salts, especially their solubilities was also planned. It was hoped that some interesting hydrates would be brought to light, in view of the close relationship existing between these sulphonates and the sulphate.

III. THE EXPERIMENTAL PART.

I. THE EXTRACTION OF CERIUM FROM ITS ORES.

The minerals used were monazite and cerite. The methods employed for the extraction of the cerium from these two ores were identical. Therefore the treatment of both will be discussed at the same time.

The finely ground mineral was treated with an excess of concentrated sulphuric acid. The pasty mass was heated in order to promote the solution of the soluble part of the ore and to remove the excess of sulphuric acid. After the mixture had been allowed to cool, it was pulverized and was then extracted with cold water, cerous sulphate being much more soluble in cold than in hot water. The extraction was continued until a few drops of the solution obtained gave no precipitate with oxalic acid or ammonium oxalate.

A preliminary test failed to show the presence of any members of the copper group of metals. Therefore the usual treatment of the solution of the soluble sulphates with hydrogen sulphide was omitted. A hot, concentrated solution of oxalic acid was then added to separate the rare earths from the iron, aluminium and calcium salts present.

It was noticed that when a hot solution of oxalic acid is added to a cold solution containing the rare earths, a yellow, dough-like mass is formed. This mass could be collected on a stirring rod. It was so viscous that it clung to the rod, even when the rod was lifted out of the solution. Since only the brief statement that a white mass is formed, when oxalic acid is added to a solution of a cerous salt, could be found, it is hoped that this point may be investigated in the near future. The yellow substance formed changed on standing for a short time to the ordinary crystalline form of the rare earth oxalates. The oxalates which precipitated were filtered, were washed and were then dried on a porous plate.

The author is indebted to Doctor H. S. Miner, of the Welsbach Company for quite a quantity of the crude oxalate, extracted from monazite and cerite. This crude oxalate was combined with that obtained from the same minerals in this laboratory. Both were subjected to the same treatment in the subsequent work.

Three methods for getting the oxalates into solution were tried.

(a) The ignition of the oxalates and the solution of the oxides so obtained in dilute nitric or sulphuric acids.

(b) The treatment of the oxalates with hot, concentrated sulphuric or nitric acid.

(c) The digestion of the oxalates with an excess of hot sodium

hydroxide solution. The hydroxides so obtained dissolved readily in dilute acids.

The first method was most satisfactory, so it was employed for the solution of the major portion of the oxalates. It has the advantage that it is more economical, since it requires no large excess of reagents. Also, by carrying on the operation in large crucibles in a muffle furnace, considerable quantities of the material can be rapidly and conveniently handled.

The solution of the oxides, prepared by the ignition of the rare earth oxalates, in nitric acid is extremely easy. The process requires only a slight excess of the reagent. After some experimentation, it was found that the addition of sulphur dioxide aided very materially both in the solution of the mixed oxides and in subsequent operations. The sulphur dioxide serves to keep the cerium in the more stable trivalent state and thus prevents any difficulty arising from the hydrolysis of the ceric salts.

The separation of the rare earths into the cerium group and the yttrium group was effected in the usual manner. Finely powdered potassium sulphate was added to the solution containing the sulphates of the rare earths. Since the double potassium sulphates of the cerium earths are insoluble in potassium sulphate, they were precipitated. This treatment left the more soluble double potassium sulphates of the yttrium earths in solution.[25] The insoluble salts were then filtered by suction, were washed with a potassium sulphate solution and were finally dried on a hot plate.

The problem of getting into solution the double sulphates which were obtained by the process just described proved to be quite a difficult one. Four different methods were employed in order to effect the solution.

(a) The digestion of the double sulphates with an excess of a hot, concentrated solution of sodium hydroxide. The addition of a dilute acid took the hydroxides formed into solution.

(b) The long-continued digestion of the salts with oxalic acid in excess. The oxalates resulting from this treatment were then taken into solution by the means of one of the methods described for the solution of the crude oxalates.[130 25]

(c) The digestion of the salts with a large excess of potassium carbonate. Dilute acids readily dissolve the carbonates so obtained. Care must be exercised not to use too great an excess of the carbonate inasmuch as the cerous carbonate is soluble in a large excess of alkali carbonate.

(d) The reduction of the double sulphates by carbon. The sulphides obtained by this reduction are dissolved in dilute acids.

The first three methods depend upon the conversion of a more

soluble into a less soluble salt, by the action of a large mass of the reagent. This process is necessarily slow and it requires a long time for its completion. If an attempt is made to conduct the reaction more rapidly by heating the vessel with the flame of a bunsen burner, a great deal of difficulty results from bumping. While this may be partially avoided by heating the surface of the liquid directly with the flame, instead of heating the vessel, even then the process is very unsatisfactory because of its slowness. The heating of the solution over a water bath or allowing it to stand on a hot plate is another means of avoiding the same troublesome bumping. But, under these conditions, the rate of reaction is also very slow.

It was found after some experimentation, that the reaction could be conducted rapidly and with great ease by employing the last mentioned method. The details of this process, as it was worked out, are essentially the following. Approximately equal parts, by volume, of powdered charcoal and the double sulphates were mixed intimately and placed in a crucible, which was then covered. The crucible and its contents were then heated for one or two hours at a full red heat in the flame of a blast lamp or in a muffle furnace. This ignition converted the sulphates into sulphides.

After the crucible had been allowed to cool for some time, its contents were slowly added to a vessel containing cold water. These precautions are absolutely necessary, since the hydrolysis of the sulphides proceeds very rapidly. The reaction is accompanied by sufficient heat to ignite the hydrogen sulphide formed, when considerable quantities of the sulphides are added at one time. Then, too, the mechanical loss due to the carrying away of the particles by the hydrogen sulphide becomes a matter of importance, if care is not taken in the addition of the sulphides.

The solution was then boiled in order to promote the hydrolysis and to expel the hydrogen sulphide formed. After a dilute solution of nitric acid had been added to complete the decomposition of the sulphides, the solution was again boiled, thus expelling the last traces of hydrogen sulphide. The excess of carbon and any sulphur which had been formed during the process were then filtered off leaving the clear solution of the nitrate.

This method is simple and very convenient. It requires no large excess of expensive reagents and consequently is very economical. In addition the rapidity with which it can be conducted is an advantage. Considerable quantities of material can be worked with in a comparatively small bulk without serious trouble. For these reasons it was employed exclusively for the transformation of the double sulphates on the large scale.

The nitrate solution so prepared was made as nearly neutral as possible by the addition of ammonium hydroxide. Hydrogen peroxide, free from phosphoric acid, was then added in order to precipitate the thorium present, as a basic nitrate.[181] The presence of a small quantity of ammonium nitrate in the solution aids in the precipitation by preventing the basic thorium nitrate from becoming colloidal. After the thorium had been filtered off, the cerium was separated from the other earths.

The ammonium persulphate method was employed for the separation and the purification of the cerium. Concentrated solutions of ammonium persulphate and sodium acetate were slowly added from dropping funnels to a boiling solution of cerous nitrate, which was kept vigorously stirred. The ammonium persulphate oxidized the cerous salt, while the sodium acetate kept the concentration of hydrogen ion very low and practically constant. Under these conditions the cerium was precipitated as a basic ceric sulphate, leaving the other cerium earths in solution. An objection to this method was that the rate of filtration was very slow. This is due both to the presence of the excess of sodium acetate and to the presence of the acetic acid formed in the reaction.

After some investigation, a modification of this method was discovered, which was free from this objection. Ammonium hydroxide was added to the boiling solution of the nitrates of the cerium earths until a slight permanent precipitate of the rare earth hydroxides was formed. When ammonium persulphate was added to this solution, the precipitation of the cerium proved to be as complete as when sodium acetate was present. The hydroxides of the rare earths formed by the addition of the ammonium hydroxide were dissolved, when the first portions of the ammonium persulphate were added. As soon as the cerous nitrate began to be oxidized, a precipitate of the basic ceric nitrate began to be formed. The addition of ammonium persulphate was continued until the precipitation was completed.

This solution possessed the advantage of being rapidly and easily filtered. Likewise no prolonged washing of the precipitate was necessary in order to free it from sodium acetate and acetic acid. The ammonium salts were present only in small quantities so that they could be easily removed by a few washings.

The ammonium persulphate method is well adapted for the purification of small quantities of cerium at a time. When the solution is not too concentrated, the separation can be made rapidly and with ease. The method is fairly complete since only a small quantity of the other earths are carried down along with the cerium.

The solution of the basic ceric nitrate was a source of difficulty and it required a large excess of nitric acid to effect this solution. After several methods had been tried, it was found that if the salt was sus-

pended in dilute nitric acid and sulphur dioxide was then added, the solution took place on standing for an hour.

The method for the separation of cerium which has just been described, was repeated until the solution showed no absorption spectrum lines. This test proved the purity of the preparation. It required three or four operations to free the cerium completely from the other cerium earths. All of the cerium, which had been purified, was converted into the sulphate. This salt was obtained in crystalline form and was then used for the preparation of the cerium compounds.

2. THE PREPARATON OF THE NEW CERIUM COMPOUNDS.

(*a*) *Cerous benzene sulphonate.* $Ce(C_6H_5SO_3)_3.9H_2O$.

(1) The preparation of barium benzene sulphonate, $Ba(C_6H_5SO_3)_2.1\frac{1}{2}\ H_2O$.

Benzene was heated on the water-bath with about five times the calculated quantity of sulphuric acid until the oily layer of benzene had disappeared.[132] This mixture was then poured into a considerable quantity of cold water. The excess of sulphuric acid and the free benzene sulphonic acid were roughly neutralized by lime. The solution was then heated to boiling, after which barium carbonate was added in order to complete the process of neutralization.[133]

The solution was separated from the barium sulphate formed by filtration and was then evaporated to a small bulk and allowed to cool. The crystals obtained were separated from the mother liquor and were then dried and analyzed for barium. The percentage of barium was found to be much less than that calculated from the formula. A qualitative analysis of the salt showed the presence of a considerable quantity of magnesium. An investigation proved that there was a high percentage of magnesium in the lime used for the rough neutralization of the acid.

Therefore the crystals were dissolved in the mother-liquor and the solution was treated with barium hydroxide in excess, in order to precipitate the magnesium present as magnesium hydroxide. The solution was filtered and the excess of barium hydroxide was removed by the addition of carbon dioxide from a Kipp generator. The solution was then boiled in order both to expel the carbon dioxide and to decompose any soluble acid barium carbonate formed. After the barium carbonate had been removed by filtration, the solution was again evaporated and allowed to cool. Large plates of barium benzene sulphonate separated out at room temperature. These crystals were removed from the mother liquor and were then dried and analyzed.

The analytical results are given in the table which follows:

For barium	I	II
gr. sample	1.0167	1.0582
gr. barium sulphate	0.4999	0.5273
% barium found	28.93	29.34
% barium calculated	29.26	29.26

All the barium salts of the sulphonic acids of benzene and its derivatives, which were employed in this study, were prepared by the digestion of the hydrocarbon with sulphuric acid. In every case the excess of acid was roughly neutralized by lime from the same source. The acids and their barium salts were all prepared before any analysis was made. Consequently the removal of the magnesium from each of the salts was necessary.

(2) The preparation of the cerium salt.

Cerous benzene sulphonate was prepared by the double decomposition of cerous sulphate and the barium salt of benzene sulphonic acid. After the barium sulphate, which had been precipitated, was separated by filtration, the solution was evaporated until crystals began to appear on the surface of the liquid. The hot solution was then allowed to cool and to crystallize at room temperature. Large, clear, six-sided plates were deposited, after the solution had stood for two or three hours. These crystals were then filtered by suction and dried between filter papers.

No difficulty was encountered in the preparation of this salt. It was only necessary to remove the barium completely, and then to evaporate the solution to crystallization.

(3) The properties of the compound.

Cerous benzene sulphonate crystallizes at room temperature in colorless, six-sided plates, which are highly hydrated. It effloresces somewhat upon exposure to the air, but it must be heated to 140° to 160° in order to dehydrate it completely. It is very soluble both in water and alcohol. Solubility measurements were conducted only for the cerous salt of m-nitrobenzene sulphonic acid. One hundred grams of water at 25° dissolve 32 grams of this salt. The cerous benzene sulphonate is considerably more soluble than the salt mentioned. The salt is so stable that it can be heated to 250° without any noticeable decomposition.

(4) The analytical results.

The method of analysis for the determination of water was to first heat the salt in a porcelain crucible to constant weight at 110°. The temperature was then raised to 140° to 160° to complete the dehydration. The anhydrous salt was then ignited in order to burn off the organic material so that the cerium could be estimated as dioxide. The

residue in the crucible was weighed as cerium dioxide and the percentage of cerium in the salt calculated on that basis. As a precaution, the cerium dioxide was then treated with a few drops of sulphuric acid. After the sulphuric acid had been expelled by heat, the crucible and contents were kept at a red heat in the blast lamp for an hour or two in order to decompose the ceric sulphate formed. The weight of cerium dioxide after this treatment served as a check on the first method.

ANALYSIS:

	I	II
For cerium		
gr. sample	1.0533	1.0127
gr. cerium dioxide	0.2359	0.2277
% cerium found	18.37	18.30
% cerium calculated	18.55	18.55
For water		
gr. sample	1.0533	1.0127
gr. loss	0.2223	0.2136
% water found	21.10	21.09
% water calculated	20.95	20.95

(*b*) *Cerous p-chlorbenzene sulphonate,* $Ce(C_6H_4ClSO_3)_3$.

(1) The preparation of barium p-chlorbenzene sulphonate, $Ba(C_6H_4ClSO_3)_2.H_2O$.

The chlorination of the benzene was carried on by allowing chlorine gas to bubble through benzene in the presence of a "halogen carrier." The increase in the weight of the benzene showed the progress of the chlorination.[134] The monochlorbenzene was washed with water for the purpose of removing the hydrochloric acid and any small quantity of ferric chloride formed. It was then distilled with steam. The distillate was further purified by drying it with calcium chloride and again subjecting it to distillation, without steam this time. The portion distilling between the limits of 129° and 135° was considered to be pure enough for the preparation of the sulphonic acid.

The p-chlorbenzene sulphonic acid was prepared in the same way and with the same relative proportions of sulphuric acid as the benzene sulphonic acid.[135] The details of the preparation of the barium salt were also the same.

ANALYSIS:

	I	II
For barium		
gr. sample	0.5158	0.5200
gr. barium sulphate	0.2249	0.2268
% barium found	25.62	25.67
% barium calculated	25.51	25.51

(2) The preparation of the cerium salt.

A number of attempts were made to prepare the cerous p-chlorbenzene sulphonate by the double decomposition method, but all of these resulted in failure. The barium was carefully removed by the addition of cerous sulphate. After the barium sulphate had been filtered off, the solution was evaporated until a white substance began to separate at its surface. The solution was then allowed to cool and to stand at room temperature. The substance which was obtained in this way was strongly acid to litmus and in every case it was quite low in its cerium content. Sometimes it contained very little cerium, and was very evidently not homogeneous.

Experiments were then made in an effort to prepare the salt by the combination of the various substances obtained with their respective mother liquors, and then the treatment of their solutions with freshly precipitated cerous carbonate or hydroxide. After long continued digestion, the excess of the cerous carbonate or hydroxide was removed by filtration, and the solution was then evaporated until a new product was obtained. The substance obtained, in all cases, was less acid in reaction, but, while the cerium content was somewhat higher, it was still too low. The digestion was repeated a number of times, but the treatment was without appreciable effect.

The method finally employed was the removal of the barium from the barium p-chlorbenzene sulphonate by means of sulphuric acid. After the removal of the barium sulphate formed, the solution containing the free p-chlorbenzene sulphonic acid was evaporated to a small bulk. An excess of freshly precipitated cerous carbonate was added to the concentrated solution, and the whole then digested on the water bath for three or four hours, or until the solution gave a neutral reaction to litmus.

The excess of cerous carbonate was next removed, after which the salt was evaporated out in the form of a white powder. On account of the very great solubility of this salt, it was found necessary to filter the solution while hot. When allowed to cool, the solution became so viscous that it was impossible to separate the salt from the mother liquor. The method just described for the preparation of cerous p-chlorbenzene sulphonate was the successful one.

(3) The properties of the salt.

The salt obtained from the hot solution was a white powder, which exhibited no crystalline structure even under the microscope. It is much more soluble in water than the analogous benzene sulphonate, and is no less soluble in alcohol than in water. This salt is also stable with respect to temperature and it can be heated to 250° without any appreciable decomposition.

(4) The analytical results.

The analysis for water was made in the same way as in the case of the analogous benzene sulphonate salt. The method of analysis for cerium differed slightly from that described for the estimation of cerium in the previous case. A few drops of sulphuric acid were first added to the water-free salt, in order to remove the chlorine and thus avoid any possible loss, due to the volatilization of cerous chloride. The crucible was then cautiously heated to expel the sulphuric acid and to burn the organic matter. It was heated at a full red heat for one or two hours in the blast lamp. The residue was weighed as cerium dioxide and the percentage of cerium calculated. The sulphuric acid treatment was then repeated to insure the complete removal of the organic matter and to serve as a check on the results first obtained.

ANALYSIS:

For cerium	I	II
gr. sample	0.5451	0.5412
gr. cerium dioxide	0.1305	0.1327
% cerium found	19.69	19.99
% cerium calculated	19.61	19.61

Owing to the difficulty of drying the salt the loss in water varied in different samples, but in no case was large enough to indicate water of crystallization.

(*c*) *Cerous p-brombenzene sulphonate,* $Ce(C_6H_4BrSO_3)_3$.

(1) The preparation of barium p-brombenzene sulphonate, $Ba(C_6H_4BrSO_3)_2$.

Brombenzene was first prepared by the slow addition of the theoretical quantity of bromine required to a flask containing benzene and finely divided iron as a halogen carrier.[136] [137] The product obtained was then washed with water, and distilled with steam. The distillate obtained was dried with calcium chloride and then purified by distillation. The portion distilling between 152° and 158° was employed in the preparation of the sulphonic acid.

The p-bromsulphonic acid and its barium salt were prepared according to the same methods which were employed in the preparation of the corresponding chlor-derivatives.[138] The method of analysis of the barium salt was exactly the same for both the p-chlorbenzene and the p-brombenzene sulphonate.

ANALYSIS:

For barium	I	II
gr. sample	0.6745	0.6205
gr. barium sulphate	0.2593	0.2403
% barium found	22.59	22.54
% barium calculated	22.54	22.54

(2) The preparation of the cerium salt.

The double decomposition method was the first one employed for the preparation of cerous p-brombenzene sulphonate. After a number of trials which proved to be unsuccessful, this method was abandoned. The cerium content was about one per cent lower than that calculated from the formula in every case, although numerous modifications were attempted. The substance obtained was repeatedly digested with cerous carbonate, but this treatment was without effect.

At last, the same process, which was necessary for the preparation of cerous p-chlorbenzene sulphonate, was employed. The barium was removed by means of sulphuric acid, and the resulting solution of the free sulphonic acid was then digested with freshly precipitated cerous carbonate. After the excess of carbonate had been removed and the solution had been evaporated until a white powder-like salt had separated, it was filtered while hot. This salt was dried between filter papers and then pulverized.

(3) The properties of the salt.

Cerous p-brombenzene sulphonate is obtained from hot solutions as a white powder, which apparently has no crystalline structure. While not so soluble in water as the analogous p-chlorbenzene sulphonate, it is more soluble than the benzene sulphonate. The salt is about as soluble in alcohol as it is in water. Like the other salts which have been described, cerous p-brombenzene sulphonate may be heated to 250° without decomposition taking place.

(4) The analytical results.

The methods for the analysis of this salt are identical with those employed for the analysis of the cerous salt of the p-chlor-derivative of benzene sulphonic acid.

ANALYSIS:

For cerium	I	II
gr. sample	0.5266	0.5685
gr. cerium dioxide	0.1082	0.1173
% cerium found	16.54	16.81
% cerium calculated	16.53	16.53

Owing to the same difficulty as in the cerous p-chlorbenzene sulphonate, the loss in water varied, but in no case indicated the presence of water of crystallization.

(*d*) *Cerous p-iodobenzene sulphonate,* $Ce(C_6H_4ISO_3)_3$.

(1) The preparation of barium p-iodobenzene sulphonate, $Ba(C_6H_4ISO_3)_2$.

Advantage was taken of the diazo reaction in the preparation of iodobenzene. A solution of aniline hydrochloride was first diazotised,

and was then heated with an aqueous solution of potassium iodide.[139] After the diazonium iodide had been allowed to decompose by standing, the iodobenzene formed was distilled with steam. The distillate was dried with calcium chloride and redistilled. That portion which distilled between 187° and 192° was taken as the pure product.

Methods, identical with those used for the preparation of other sulphonates, were employed for the preparation of barium p-iodobenzene sulphonate.[140]

ANALYSIS:

For barium	I	II
gr. sample	0.5034	0.5480
gr. barium sulphate	0.1664	0.1812
% barium found	19.44	19.36
% barium calculated	19.53	19.53

(2) The preparation of the cerium salt.

Cerous p-iodobenzene sulphonate was prepared by the double decomposition method, somewhat modified. The first efforts to obtain the salt were without success, a product separating out which was pronouncedly acid to litmus. In one case, crystals of almost pure p-iodobenzene sulphonic acid were obtained. However, it was discovered that by a long continued digestion of these crystals, dissolved in the mother liquor, with cerous carbonate in excess, the normal salt could be isolated upon the evaporation of the solution so prepared.

(3) The properties of the salt.

Cerous p-iodobenzene sulphonate is a white salt which, when obtained from the solution at room temperature, seems to be non-crystalline. It is less soluble both in water and in alcohol than the corresponding p-chlor-and p-bromsulphonates. The salt is very stable and does not decompose, when heated to 250°.

(4) The analytical results.

The salt was analyzed in the same way as the p-chlor- and p-brom-salts.

ANALYSIS:

For cerium	I	II
gr. sample	0.5805	0.7357
gr. cerium dioxide	0.1020	0.1268
% cerium found	14.29	14.03
% cerium calculated	14.17	14.17

The loss on heating indicated that no water of crystallization was present in the salt.

(e) Cerous m-nitrobenzene sulphonate, $Ce(C_6H_4NO_2SO_3)_3.6H_2O$.

(1) The preparation of barium m-nitrobenzene sulphonate, $Ba(C_6H_4NO_2SO_3)_2.H_2O$.

Nitrobenzene was heated on a water-bath with five times the calculated quantity of a mixture of one part of fuming to two parts of ordinary concentrated sulphuric acid, until the oily layer disappeared. These proportions proved, by experiment, to be the most favorable. A less concentration of the fuming acid caused the reaction to proceed very slowly, while a greater concentration produced enough heat of reaction to decompose the hydrocarbon.[141] The preparation of the barium salt of this acid was carried on according to the process already described.

ANALYSIS:

For barium	I	II
gr. sample	0.7849	1.0282
gr. barium sulphate	0.3293	0.4300
% barium found	24.69	24.61
% barium calculated	24.55	24.55

(2) The preparation of the cerium salt.

The cerium m-nitrobenzene sulphonate was prepared by the double decomposition method without any difficulty. The details of this method have been described in the preparation of cerous benzene sulphonate. Upon allowing the solution to stand at room temperature, pale yellow crystals of the salt were obtained. These crystals were separated by filtration and then dried between filter papers.

(3) The properties of the salt.

The six-sided plates of this salt are pale yellow in color and they contain six molecules of water of crystallization. As has been stated, about 32 grams of this salt dissolve in 100 grams of water at 25°. It is also very soluble in water. The salt effloresces only very slightly upon exposure to the air and loses all its water of crystallization at 160°. Cerous m-nitrobenzene sulphonate is less stable toward heat than the salts already described. It begins to discolor at about 200° and decomposes slowly above that temperature.

(4) The analytical results.

The methods employed in the analysis of this salt were the same as those used in the analysis of cerous benzene sulphonate. Considerable care was necessary in the ignition of the organic matter, since the combustion was very rapid, when once the kindling temperature had been reached. The cerium dioxide left after the ignition was weighed and then moistened with sulphuric acid. This acid was expelled by heat and the residue heated in a blast lamp for an hour or two. The cerium dioxide remaining was again weighed as a check in the first weight obtained.

ANALYSIS:

For cerium	I	II
gr. sample	0.6393	0.8204
gr. cerium dioxide	0.1308	0.1675
% cerium found	16.67	16.60
% cerium calculated	16.41	16.41

For water	I	II
gr. sample	1.1415	1.0137
gr. loss	0.1405	0.1241
% water calculated	12.30	12.24
% water found	12.64	12.64

(f) Cerous p-toluene sulphonate, $Ce(C_6H_4CH_3SO_3).11H_2O$.

(1) The preparation of barium p-toluene sulphonate, $Ba(C_6H_4CH_3SO_3)_2$.

Barium p-toluene sulphonate was prepared by methods analogous to those already described.[142] The slow change of a powder-like form of this salt into a crystalline modification, upon its standing for a week in contact with the mother liquor was observed. It is hoped that an investigation in the near future will clear up this point.

ANALYSIS:

For barium	I	II
gr. sample	0.5431	0.5004
gr. barium sulphate	0.2634	0.2425
% barium found	28.56	28.51
% barium calculated	28.64	28.64

(2) The preparation of the cerous salt.

Without the slightest difficulty, the cerous p-toluene sulphonate was obtained by the double decomposition method. Upon the evaporation of the solution, colorless crystals of the salt separated out, after standing for an hour or two at room temperature.

(3) The properties of the salt.

Cerous p-toluene sulphonate is a beautifully crystalline salt, forming small colorless needles. It is highly hydrated and readily effloresces when exposed to the air. Like the other cerous sulphonates described, it is dehydrated completely at 160° and is very stable towards heat. It is more soluble in water than either its benzene or its m-nitrobenzene analogues.

(4) The analytical results.

The analysis of this salt was conducted in precisely the same way as that of cerous benzene sulphonate.

ANALYSIS:

For cerium	I	II
gr. sample	0.5139	0.8810
gr. cerium dioxide	0.1036	0.1770
% cerium found	16.40	16.36
% cerium calculated	16.46	16.46
For water		
gr. sample	0.5139	0.7088
gr. loss	0.1206	0.1659
% water found	23.46	23.40
% water calculated	23.26	23.26

(*g*) *Cerous p-phenol sulphonate,* $Ce(C_6H_4OHSO_3)_3.7\frac{1}{2}H_2O$.

(a) The preparation of barium p-phenol sulphonate, $Ba(C_6H_4OHSO_3)_2.4H_2O$.

Kekule[143] states that if a solution of the theoretical quantities of sulphuric acid and phenol are heated together at 110° for a long time, only the para acid is formed. The acid so prepared, was neutralized according to the previously described methods.

ANALYSIS:

For barium	I	II
gr. sample	1.0688	1.0124
gr. barium sulphate	0.4501	0.4467
% barium found	24.79	24.80
% barium calculated	24.71	24.71

(2) The preparation of the cerium salt.

The usual mode of procedure was followed in the preparation of the cerium salt. The rate of crystallization from the saturated solution at room temperature was so slow, that it was found quite advantageous to surround the solution by a freezing mixture. The change in solubility from room temperature to that of a freezing mixture is very great. Consequently, a considerable crop of crystals could easily be obtained by this method. Crystallization at a higher temperature was also attempted, but the product was a sort of crystal meal, which was not convenient to handle. The salt was prepared for analysis in the usual way.

(3) The properties of the salt.

Cerous p-phenol sulphonate forms colorless needles, when crystallized from a cold solution. These crystals are very highly hydrated. They effloresce less rapidly than cerous p-toluene sulphonate upon exposure to the air. The salt is completely dehydrated by heating at 160°. It is very soluble in hot water, and in cold water it is about as soluble as the corresponding cerous m-nitrobenzene sulphonate. It is also quite soluble in alcohol. This salt is as stable as the other cerous sulphonates.

(4) The analytical results.

The analytical processes employed were those already described.

ANALYSIS:

For cerium	I	II
gr. sample	0.5272	0.5088
gr. cerium dioxide	0.1140	0.1103
% cerium found	17.60	17.64
% cerium calculated	17.68	17.68
For water		
gr. sample	0.8977	0.5272
gr. loss	0.1543	0.6910
% water found	17.18	17.24
% water calculated	17.00	17.00

3. THE PREPARATION OF THE NEW LANTHANUM COMPOUNDS.

The lanthanum salts of the same sulphonic acids were prepared in an analogous way. All were prepared by the double composition of lanthanum sulphate and the barium salt of the sulphonic acid, excepting the p-chlor- and p-brom-sulphonates. These two salts were prepared in the same way as their cerium analogues namely, by the digestion of the free acid with lanthanum carbonate. The lanthanum sulphate used was prepared from a sample of pure lanthanum ammonium nitrate, for which the author is indebted to Doctor H. S. Miner of the Welsbach Company.

The method employed for the estimation of lanthanum was the precipitation of the lanthanum as hydroxide by ammonium hydroxide. The hydroxide was separated by filtration, dried, and then ignited to dehydrate it, thus forming lanthanum oxide. This mode of procedure was necessary, owing to the fact that lanthanum sulphate cannot be decomposed except by prolonged heating. The water content was determined by the loss in weight at 160° in an air bath.

(*a*) *Lanthanum benzene sulphonate,* $La(C_6H_5SO_3)_3.9H_2O$.

This salt crystallizes in large, colorless, six sided plates, similar to those formed by its cerium analogue. Its properties are very similar to those of cerous benzene sulphonate.

ANALYSIS:

For lanthanum	I	II
gr. sample	0.4083	0.6440
gr. lanthanum oxide	0.0773	0.1225
% lanthanum found	16.14	16.21
% lanthanum calculated	15.93	15.93
For water	I	II
gr. sample	0.4083	0.6201
gr. loss	0.0765	0.1183
% water found	18.69	19.07
% water calculated	18.57	18.57

(b) Lanthanum p-chlorbenzene sulphonate, $La(C_6H_4ClSO_3)_3$

The preparation and properties of this salt are the same as in the case of the corresponding cerous salt. It can be prepared somewhat more easily, however, owing to the more ready solubility of lanthanum carbonate in dilute acids.

ANALYSIS:

For lanthanum	I	II
gr. sample	0.4844	0.4850
gr. lanthanum oxide	0.1078	0.1089
% lanthanum found	18.99	19.15
% lanthanum calculated	19.47	19.47

No water of crystallization was found.

(c) Lanthanum p-brombenzene sulphonate, $La(C_6H_4BrSO_3)_3$.

The same difficulties of preparation were encountered in the preparation of the salt, as in the preparation of cerous p-brombenzene sulphonate. The properties of the two are nearly identical.

ANALYSIS:

For lanthanum	I	II
gr. sample	0.4889	0.5665
gr. lanthanum oxide	0.0820	0.0947
% lanthanum found	14.38	14.26
% lanthanum calculated	14.07	14.07

(d) Lanthanum p-iodobenzene sulphonate, $La(C_6H_4ISO_3)_3$.

This white powder-like salt is prepared in the same way as the cerous salt. The same difficulty of an acid substance separating out was encountered. This was avoided, as in the preparation of the cerous salt, by the digestion of the solution with lanthanum carbonate. The lanthanum and the cerous salts are very similar both in physical and in chemical properties.

ANALYSIS:

For lanthanum	I	II
gr. sample	0.6001	0.5131
gr. lanthanum oxide	0.1007	0.0838
% lanthanum found	14.30	13.93
% lanthanum calculated	14.07	14.07

(e) Lanthanum m-nitrobenzene sulphonate, $La(C_6H_4NO_2SO_3)_3.6H_2O$.

Small six-sided plates of this salt, which closely resembles the cerous salt were obtained. Its properties are similar to those already described for the cerous salt.

ANALYSIS:

For lanthanum	I	II
gr. sample	0.5673	0.9445
gr. lanthanum	0.1036	0.1863
% lanthanum found	16.39	16.81
% lanthanum calculated	16.28	16.28
For water		
gr. sample	0.9757	0.7748
gr. loss	0.1167	0.0938
% water found	12.16	12.11
% water calculated	12.66	12.66

(*f*) *Lanthanum p-toluene sulphonate,* $La(C_6H_4CH_3SO_3)_3.12H_2O$.

This salt is very similar to its cerium analogue.

ANALYSIS:

For lanthanum	I	II
gr. sample	0.7150	0.4926
gr. lanthanum oxide	0.1343	0.0890
% lanthanum found	16.01	15.41
% lanthanum calculated	16.00	16.00
For water		
gr. sample	0.5843	0.6465
gr. loss	0.1441	0.1605
% water found	24.68	24.82
% water calculated	24.89	24.89

(*g*) *Lanthanum p-phenol sulphonate,* $La(C_6H_4OHSO_3)_3.7\frac{1}{2}H_2O$.

Crystals of this salt, similar to the corresponding salt cerium salt both in physical and chemical properties, were obtained from a solution of salt, cooled by a freezing mixture.

ANALYSIS:

For lanthanum	I	II
gr. sample	0.6465	0.5256
gr. lanthanum oxide	0.1345	0.1090
% lanthanum found	17.83	17.67
% lanthanum calculated	17.52	17.52
For water		
gr. sample	0.5076	0.5256
gr. loss	0.0851	0.0889
% water found	16.79	16.93
% water calculated	17.03	17.03

SUMMARY.

I. The methods for the extraction of cerium were critically reviewed and some of the steps were modified.

II. The cerous and lanthanum sulphonates of benzene and some of its derivatives were prepared and a preliminary study of their properties was made.

III. Some interesting observations on the nature of the salts were made, which offer an opportunity for future investigation.

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